

Chlorinated Paraffins (C₁₂, 60% Chlorine)

CAS No. 108171-26-2

Reasonably anticipated to be human carcinogens

First listed in the *Fifth Annual Report on Carcinogens* (1989)

Carcinogenicity

Chlorinated paraffins (C₁₂, 60% chlorine) are *reasonably anticipated to be human carcinogens* based on sufficient evidence of carcinogenicity from studies in experimental animals.

Cancer Studies in Experimental Animals

Oral exposure to chlorinated paraffins (C₁₂, 60% chlorine) caused tumors at several different tissue sites in mice and rats. Administration of chlorinated paraffins by stomach tube increased the combined incidence of benign and malignant liver tumors (hepatocellular adenoma and carcinoma) in mice of both sexes, the thyroid gland (follicular-cell adenoma and carcinoma) in female mice and rats, and the kidney (tubular-cell adenoma and carcinoma) in male rats. It also caused benign liver tumors (hepatocellular adenoma) in rats of both sexes and possibly mononuclear-cell leukemia in male rats (NTP 1986).

Cancer Studies in Humans

No epidemiological studies were identified that evaluated the relationship between human cancer and exposure specifically to chlorinated paraffins (C₁₂, 60% chlorine). Since chlorinated paraffins were listed in the *Fifth Annual Report on Carcinogens*, a registry-based case-control study of cancer of the liver and biliary tract in auto-workers has been identified (Bardin *et al.* 2005). The case-control study was nested in a cohort study of autoworkers exposed to metalworking fluids. Exposure to specific metalworking fluid components and additives was evaluated, and any exposure to chlorinated paraffins (type not specified) was associated with elevated risk of biliary-tract cancer, based on a small number of cases. No increased risk was found for liver cancer; however, the study included only one exposed worker with liver cancer.

Properties

Chlorinated paraffins are chlorinated long-chain aliphatic compounds. They exist as light-yellow to amber-colored viscous, oily liquids that are usually odorless. The commercial products are complex mixtures that contain paraffins with various carbon-chain lengths and varying chlorine content. The commercial products normally contain stabilizers to inhibit decomposition and may contain isoparaffins (< 1%), aromatic compounds (< 0.1%), and metals as contaminants. Chlorinated paraffins are practically insoluble in water, but many products may be emulsified with water. They are miscible with benzene, chloroform, ether, and carbon tetrachloride, slightly soluble in alcohol, and soluble in most aromatic, aliphatic, and terpene hydrocarbons, ketones, esters, and vegetable and animal oils. Chlorinated paraffins have low volatility and are nonflammable. When heated to decomposition, they emit toxic fumes of hydrochloric acid and other chlorinated compounds. The physical and chemical properties of these chemical mixtures are variable. The octanol-water partition coefficient (log *K*_{ow}) ranges from 4.48 to 7.38 (IPCS 1996, HSDB 2009).

Use

Chlorinated paraffins are used as extreme-pressure-lubricant additives in metalworking fluids; as flame retardants in plastics, rubber, and paints; to improve water resistance of paints and fabrics; and as a secondary plasticizer in polyvinyl chloride. Small amounts are also

used in caulks, sealants, adhesives, detergents, inks, finished leather, and other miscellaneous products, and are allowed as an indirect food additive (NTP 1986, CMR 2002, HSDB 2009, FDA 2010). In the United States, about 50% of chlorinated paraffins are used in metalworking fluids, 20% in plastics additives, 12% in rubber, 9% in coatings, 6% in adhesives, caulks, and sealants, and the remaining 3% for miscellaneous purposes (CMR 2002). Chlorinated paraffins have replaced polychlorinated biphenyls as fire-retardant lubricants (NTP 1986). Between 1914 and 1918, large amounts of chlorinated paraffins were used as solvents for dichloramine-T in antiseptic nasal and throat sprays (IPCS 1996).

Production

Commercial production of chlorinated paraffins for use as additives in extreme-pressure lubricants began in the 1930s. Global production reached 250,000 metric tons (over 550 million pounds) in 1978 but declined to 99 million pounds in 1983. In 2002, the two U.S. manufacturers reported an annual production capacity of 140 million pounds. Demand for chlorinated paraffins remained relatively steady from 1983 to 2009, at 96 million to 100 million pounds (NTP 1986, IARC 1990, CMR 2002). In 2009, chlorinated paraffins were produced by 78 manufacturers worldwide, including 2 in the United States, 40 in China, and 22 in India (SRI 2009). No specific data on U.S. imports or exports of chlorinated paraffins were found.

Exposure

No information on potential human exposure specifically to chlorinated paraffins (C₁₂, 60% chlorine) was found, but information was available on potential human exposure to the class of chlorinated paraffins. The routes of potential human exposure include inhalation, dermal contact, and ingestion, primarily through contamination of foods (IPCS 1996). Because chlorinated paraffins are permitted in adhesives used in food packaging, the general population could be exposed to very low concentrations through ingestion of contaminated food products wrapped in these materials (FDA 2010). Short-chain chlorinated paraffins (SCCPs) (C₁₀ to C₁₃) have also been found in food products contaminated through environmental exposure. In Japan, SCCPs were found in high-lipid-content foods such as dairy products, vegetable oil, salad dressing, and mayonnaise, at a mean concentration of 140 ng/g of wet weight (Bayen *et al.* 2006). The next-most-contaminated Japanese food category was fish and shellfish, with SCCP concentrations of 16 to 18 ng/g of wet weight. The levels in Japanese foods would translate to an average daily intake of 680 ng/kg of body weight for a 1-year-old female infant in Japan (the highest rate reported). In European butter samples, SCCPs were measured at concentrations of 1.2 to 2.7 µg/kg of lipid content. In addition, chlorinated paraffins have been isolated from human tissues, including liver, kidney, and adipose tissue, at concentrations of up to 1.5 mg/kg of wet tissue (most values were < 0.09 mg/kg) (Campbell and McConnell 1980), and from breast milk at concentrations up to 0.8 mg/kg of milk fat (Thomas *et al.* 2006).

Chlorinated paraffins are lipophilic and persistent in the environment. The very low vapor pressure indicates that these compounds will not volatilize easily. If released to air, they will exist as particulates and will not remain in the atmosphere; they may be photochemically degraded, with a half-life of 1.2 to 1.8 days (IPCS 1996). Chlorinated paraffins have been measured in the atmosphere in the United Kingdom at concentrations of up to 3.4 ng/m³ (Barber *et al.* 2005).

Chlorinated paraffins have low water solubility and a high log *K*_{ow}. Therefore, if released to water, they will not volatilize from water or remain in solution, but will adsorb to sediment or suspended solid material. If released to soil, chlorinated paraffins are bound to the soil

particles and are not expected to volatilize or to leach into ground-water. Based on limited data, chlorinated paraffins do not biodegrade readily (IPCS 1996, HSDB 2009). In 1988, chlorinated paraffins were measured in the United States in water, sediment, and aquatic organisms downstream from industrial facilities where chlorinated paraffins were made or used. The concentrations measured were less than 8 µg/L in water (compared with < 0.3 µg/L upstream from the same facility) and up to 40 mg/kg in sediment. SCCP concentrations measured in Lake Ontario sediment cores in 1998 averaged 49 µg/kg. Maximum SCCP concentrations in the sediment cores increased from less than 50 µg/kg in 1900 to over 800 µg/kg in the 1980s and then declined to 410 µg/kg in 1998 (Marvin *et al.* 2003). These data are consistent with a maximum concentration of 347 µg/kg in sediment samples collected in the Czech Republic in 2003 (Pribylova *et al.* 2006). In 1980, short- and medium-chain chlorinated paraffins were measured in non-industrialized areas of the United Kingdom at concentrations up to 1 µg/L in water and up to 1 mg/kg in sediment; in industrialized areas, measured concentrations in sediment were as high as 15 mg/kg (Campbell and McConnell 1980). Marine samples collected away from land in the North and Baltic Seas from 2001 to 2003 contained SCCPs at concentrations of up to 377 µg/kg (Huttig and Oehme 2005).

Aquatic organisms were found to contain chlorinated paraffins (C₁₀ to C₂₀) at concentrations similar to those in sediment; for example, a mean concentration of 3.25 mg/kg was found in mussels collected in the United Kingdom (Campbell and McConnell 1980). Chlorinated paraffins potentially may bioaccumulate in some animal species (IPCS 1996, Huttig and Oehme 2005); however, they do not biomagnify in the food chain (Madeley and Birtley 1980). They were also measured in the blubber of marine mammals at concentrations of 0.164 to 1.4 µg/kg and in the fat of terrestrial wildlife at up to 4.4 mg/kg (IPCS 1996).

Occupational exposure is likely in production plants or in industries using chlorinated paraffins (IPCS 1996). In facilities using metalworking fluids containing chlorinated paraffins for milling, cutting, and grinding, aerosol concentrations of up to 1.15 mg/m³ were reported; however, it is not known whether chlorinated paraffin aerosols are in the inhalable size range. Dermal exposure of the hands and forearms was predicted to range from 0.1 to 1 mg/cm² per day for production of chlorinated paraffins and up to 1.5 mg/cm² for their use as metalworking fluids. The National Occupational Exposure Survey (conducted from 1981 to 1983) estimated that 573,193 workers, including 38,354 women, potentially were exposed to substances in the category “Paraffin, chlorinated (CAS 63449-39-8, Paraffin waxes and hydrocarbon waxes)” and that 61,464 workers, including 3,717 women, potentially were exposed to substances in the smaller category of “Chlorinated paraffin” (NIOSH 1990).

Regulations

Department of Transportation (DOT)

Chlorinated paraffins are considered marine pollutants, and special requirements have been set for marking, labeling, and transporting these materials.

Food and Drug Administration (FDA)

Chlorinated paraffins are allowed for use as indirect additives used in food contact substances as prescribed in 21 CFR 175 and 177.

Occupational Safety and Health Administration (OSHA)

While this section accurately identifies OSHA's legally enforceable PELs for this substance in 2010, specific PELs may not reflect the more current studies and may not adequately protect workers. Permissible exposure limit (PEL) = 5 mg/m³ for paraffin oil mist.

Guidelines

National Institute for Occupational Safety and Health (NIOSH)

Immediately dangerous to life and health (IDLH) limit = 2,500 mg/m³ for paraffin oil mist.
Recommended exposure limit (REL) = 5 mg/m³ for paraffin oil mist.
Short-term exposure limit (STEL) = 10 mg/m³ for paraffin oil mist.

References

- Barber JL, Sweetman AJ, Thomas GO, Braekevelt E, Stern GA, Jones KC. 2005. Spatial and temporal variability in air concentrations of short-chain (C₁₀–C₁₃) and medium-chain (C₁₄–C₁₇) chlorinated n-alkanes measured in the U.K. atmosphere. *Environ Sci Technol* 39(12): 4407–4415.
- Bardin JA, Gore RJ, Wegman DH, Kriebel D, Woskie SR, Eisen EA. 2005. Registry-based case-control studies of liver cancer and cancers of the biliary tract nested in a cohort of autoworkers exposed to metalworking fluids. *Scand J Work Environ Health* 31(3): 205–211.
- Bayen S, Obbard JP, Thomas GO. 2006. Chlorinated paraffins: a review of analysis and environmental occurrence. *Environ Int* 32(7): 915–929.
- Campbell I, McConnell G. 1980. Chlorinated paraffins and the environment: environmental occurrences. *Environ Sci Technol* 14(10): 1209–1214.
- CMR. 2002. Chemical profile – chloroparaffins. *Chem Mark Rep* 9/2/02. ICIS. <http://www.icis.com/Articles/2005/12/02/180012/Chemical-Profile-Chloroparaffins.html>.
- FDA. 2010. *Indirect Food Additives: Adhesives and Components of Coatings*. 21 CFR 175. Electronic Code of Federal Regulations. <http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&sid=d36753bca57802e9889f3bc4f277c77e&rgn=div5&view=text&node=21:3.0.1.1.6&idno=21#21:3.0.1.1.6.2>.
- HSDB. 2009. *Hazardous Substances Data Bank*. National Library of Medicine. <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB> and search on CAS number. Last accessed: 5/09.
- Huttig J, Oehme M. 2005. Presence of chlorinated paraffins in sediments from the North and Baltic Seas. *Arch Environ Contam Toxicol* 49(4): 449–456.
- IARC. 1990. Chlorinated paraffins. In *Some Flame Retardants and Textile Chemicals and Exposures in the Textile Manufacturing Industry*. IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans, vol. 48. Lyon, France: International Agency for Research on Cancer. pp. 55–72.
- IPCS. 1996. *Environmental Health Criteria 181. Chlorinated Paraffins*. International Programme on Chemical Safety. <http://www.inchem.org/documents/ehc/ehc/ehc181.htm>.
- Madeley JR, Birtley RDN. 1980. Chlorinated paraffins and the environment. II. Aquatic and avian toxicology. *Environ Sci Technol* 14(10): 1215–1221.
- Marvin CH, Painter S, Tomy GT, Stern GA, Braekevelt E, Muir DC. 2003. Spatial and temporal trends in short-chain chlorinated paraffins in Lake Ontario sediments. *Environ Sci Technol* 37(20): 4561–4568.
- NIOSH. 1990a. *National Occupational Exposure Survey (1981–83)*. National Institute for Occupational Safety and Health. <http://www.cdc.gov/noes/noes1/x5417sic.html>.
- NIOSH. 1990b. *National Occupational Exposure Survey (1981–83)*. National Institute for Occupational Safety and Health. <http://www.cdc.gov/noes/noes1/x8345sic.html>.
- NTP. 1986. *Toxicology and Carcinogenesis Studies of Chlorinated Paraffins (C12, 60% Chlorine) (CAS No. 63449-39-8) in F344/N Rats and B6C3F₁ Mice (Gavage Studies)*. NTP Technical Report Series no. 308. Research Triangle Park, NC: National Toxicology Program. 223 pp.
- Pribylova P, Klanova J, Holoubek I. 2006. Screening of short- and medium-chain chlorinated paraffins in selected riverine sediments and sludge from the Czech Republic. *Environ Pollut* 144(1): 248–254.
- SRI. 2009. *Directory of Chemical Producers*. Menlo Park, CA: SRI Consulting. Database edition. Last accessed: 5/09.
- Thomas GO, Farrar D, Braekevelt E, Stern G, Kalantzi OI, Martin FL, Jones KC. 2006. Short and medium chain length chlorinated paraffins in U.K. human milk fat. *Environ Int* 32(1): 34–40.